Vulcanized Acrylic Resins

COPOLYMERS OF ETHYL ACRYLATE AND ALLYL MALEATE

Rubberlike materials were made by copolymerizing emulsified ethyl acrylate with small proportions of allyl maleate and vulcanizing the resulting unsaturated acrylic resins with sulfur and accelerators and with other agents in the absence of sulfur. Acrylonitrile (preferably about 6%) and dodecyl mercaptan had a beneficial effect, possibly because of their tendency to decrease cross linkage. Ammonium persulfate was preferable as polymerization catalyst; a small amount caused polymerization to proceed smoothly. Benzoyl peroxide was also effective but produced properties, such as insolubility and toughness, that are sometimes attributed to cross linkage. Although not so active as benzoyl peroxide, hydrogen peroxide was moderately satisfactory. Sodium perborate had no advantage. Nonsulfur vulcanization gave promising results. Combinations of quinone dioxime, quinone dioxime dibenzoate, red lead, and lead peroxide produced vulcanizates with considerably higher tensile strength and somewhat greater hardness than did sulfur.

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BECAUSE of their flexibility and certain rubberlike characteristics, acrylic resins have been used in place of rubber for some purposes (*4*, *6*, *7*). Since it seemed reasonable that the value of acrylic resins as rubber replacements would be enhanced by vulcanization, an investigation of the preparation and properties of vulcanized or cross-linked acrylic polymers was inaugurated in this Laboratory. An earlier paper (*2*) described preliminary results, which showed that vulcanizable polymers could be prepared by copolymerizing acrylic esters with small proportions of polyfunctional monomers such as butadiene, isoprene, and allyl maleate. The copolymers prepared were compounded with sulfur, vulcanization accelerators, and carbon black, and vulcanized with the equipment and techniques ordinarily used in processing natural and synthetic rubbers. These vulcanizates were more rubberlike than the unvulcanized acrylic resins and appeared to warrant further study.

The present paper describes the results of investigating certain variables in the production of vulcanized acrylic resins. To simplify the study and decrease the numerous possibilities afforded in copolymerization, compounding, and curing operations, ethyl acrylate and allyl maleate were selected as the acrylic and polyfunctional monomers. Ethyl acrylate was chosen because its polymers are softer and more rubbery than the other acrylic resins examined in the preliminary study. To provide information on suitable monomer concentrations and conditions of polymerization, uniform compounding and curing conditions were used in most experiments.

The monomers were emulsion-polymerized because this operation can be carried out conveniently both in the laboratory and plant, and also because emulsion polymerization ordinarily yields polymers of relatively high molecular weight. Hydrogen peroxide (27.5%) and benzoyl peroxide were used to initiate polymerization in the earlier experiments, but ammonium persulfate was employed after its advantages as catalyst were discovered.

Satisfactory copolymers were prepared with Triton K 60 (*10*) as emulsifying agent and hydrogen peroxide as catalyst, but an appreciable amount of polymer was usually precipitated during this reaction, necessitating the laborious removal of resin from the stirrer and vessel. Controlling the rate of polymerization offered some difficulties when hydrogen peroxide was used. Triton K 60 could not be employed with ammonium persulfate or sodium perborate catalysts because of precipitation or loss of emulsifying action.

Tergitol Penetrant No. 4 (*10*) worked satisfactorily with ammonium persulfate, sodium perborate, benzoyl peroxide, or hydrogen peroxide. Little if any polymer precipitated from the emulsion during polymerization. Moreover, the polymer emulsion could be completely broken merely by adding a dilute solution of sodium chloride.

Acrylonitrile and dodecyl mercaptan were used in some of the experiments to decrease or prevent cross linkage (*1*). Polymerization seemed easier to control in the presence of dodecyl mercaptan when hydrogen peroxide was used as catalyst.

The copolymers were prepared, compounded, cured, and

Table I. Effect of Allyl Maleate and Acrylonitrile

Expt. No.	Monomers, Grams: Ethyl acrylate	Acrylonitrile	Allyl maleate	Dodecyl Mercaptan, G.	Water, Ml.	Triton K 60, G.	Tergitol No. 4, G.	Catalyst: H₂O₂, ml.	Benzoyl peroxide, g.	Ammonium persulfate, g.	Polymerization: Temp., ° C.	Time, hr.	Yield, %	Vulcanization: Time, min.	Temp., ° C.	Tensile Strength, Lb./Sq. In.	Elongation, %	Shore A Hardness	Brittle Point, ° C.	Tensile Product	% Gain in Weight after Immersion in: Toluene-heptane	Water
1	98	1	1	0.1	300	1.5	0	18.7	0	0	65.6	5.25	90	180	148	640	1500	48	−15	960	26	..
2	96	2	2	0.1	300	1.5	0	18.7	0	0	65.6	5.25	93	120	148	400	790	45	−12	316	23.8	..
3	94	3	3	0.1	300	1.5	0	12	0	0	65.6	8.5	90	90	148	600	610	45	−12	366	20.7	..
4	90	5	5	0.1	300	1.5	0	12	0	0	65.6	5.25	89	120	148	710	360	48	− 7	256	20.5	..
5[a]	90	5	5	0	150	2	0	3.5	0	0	82–92	6.75	..	120	148	990	490	47	− 8	484	17.2	3.5
6[a]	180	10	10 (5%)	0.5	250	2	..	2.5	0	0	82–92	1.08	..	120	148	760	960	48	−11	730	14.2	5.8
7[b]	80	10	10	0.1	300	1.5	0	12	0	0	65.6	6.5	83	..	..	..	..	..	..	..	..	..
8[b]	60	20	20	0.1	300	1.5	0	32	1	0	65.6	8	94	..	..	..	..	..	..	..	..	..
9	97	0	3	0.1	300	1.5	0	22	0	0	65.6	5.5	90	240	148	300	430	50	−10	129	26[c]	..
10	97	0	3	0	300	1.5	0	45	0.5	...	65.6	11.5	95	..	..	..	..	..	..	..	..	..
11	94	3	3	0.1	300	0	2	2.35	0	0	82–92	1.75	93	180	148	690	620	55	−14	427	24.7	..
12	94	3	3	0	300	1.5	0	30	0.5	0	65.6	8.75	91	240	148	560	440	54	− 8	247	21.5	..
13	92	5	3	0.1	300	1.5	0	17	0	0	65.6	6.25	95	120	148	600	860	35	− 9	516	13	..
14	318.5	21	10.5 (3%)	0.25	1050	0	7	0	0	0.03	83–91	5	94	180	148	850	770	55	−12	654	..	..
15	91	6	3	0.1	300	1.5	0	30	0	0	65.6	9	90	180	148	870	660	59	− 7	574	17	..
16[d]	88	9	3	0.1	300	1.5	0	25	0	0	65.6	5	..	..	..	..	..	..	..	..	..	..
17[d]	88	9	3	0	300	1.5	0	25	0	0	65.6	6	96	..	..	..	..	..	..	..	..	..
18[e]	88	9	3	0.1	300	0	2	0	0	0.1	82–92	0.5	90	180	148	1180	470	53	..	531	19.3	..
19[f]	82	15	3	0.1	300	0	2	0	0	0.055	75–92	3.33	86.5	120	148	1510	370	80	0	558	19.8	..
20[g]	73	24	3	0.1	300	0	2	0	0	0.050	75–92.5	2.67	87.5	180	148	1640	250	89	+24	410	14.5	..
21[g]	62	35	3	0.1	300	0	2	0	0	0.055	75–91	4.83	88.7	..	..	..	..	..	..	..	..	..
22	98	0	2	0	150	2	0	0.5	0	0	82–92	0.92	80	80	148	510	700	41	..	357	20	1.6
23	99.5	0	5 (4.8%)	0	150	2	0	0.5	0	0	82–92	0.75	83	80	148	340	380	48	..	129	8.5	..
24	95	0	5	0.5[h]	150	2	0	2	0	0	82–92	0.67	..	120	148	380	570	46	−19	201	16.3	3.5
25	95	0	5	0.25	150	2	0	2	0	0	82–92	1.0	..	120	148	330	390	48	..	128	..	..
26	475	0	25 (5%)	1.0	600	6	0	1	0	0	82–92	2.33	..	120	148	320	400	45	..	128	..	..
27[a,i]	500	0	55 (10%)	..	700	8.5	0	5.5	0	0	82–92	0.5	..	140	146	360	300	48	..	108	..	..

[a] Reported in another paper (2). [b] Copolymer was inelastic. [c] Specimen was weakened. [d] Copolymer was soft and taffylike. [e] About one third of the mixture foamed out of the flask. [f] Copo lymer was hard and slightly rubbery. [g] Copolymer was hard and inelastic. [h] Mercaptan 3B, 0.5 gram. [i] Forty parts of black was used.

tested as described previously (2). The following ingredie were used (parts per 100 parts of polymer): Captax (merca benzothiazole), 0.5; zinc oxide, 5; stearic acid, 2; sulfur, Furnex Beads (carbon black), 30; and Tuads (tetramethylthiura disulfide), 1. Tensile product was calculated from the formula:

$$\text{tensile product} = \frac{(\text{tensile strength})\ (\text{elongation})}{1000}$$

Copolymers prepared in the present work were incompletely soluble at room temperature in several common organic solvents, possibly because of cross linkage. Hence, data on molecular weight based on viscosity measurements would be difficult to obtain and of questionable significance. A relation has been observed (8), however, between the swelling characteristics of the insoluble fraction and the viscosity of solutions of the soluble fraction for styrene-butadiene copolymers.

EFFECT OF ALLYL MALEATE AND ACRYLONITRILE

The copolymers prepared from a monomer mixture containing as little as 1% allyl maleate (Table I, experiment 1) were found to be vulcanizable with sulfur and accelerators. When used with an equal quantity of acrylonitrile, the following changes in properties of the vulcanizate occurred as the proportion of allyl maleate was increased to 5% (experiments 1 to 5): The amount of hydrocarbon mixture (50% toluene–50% heptane) sorbed by the

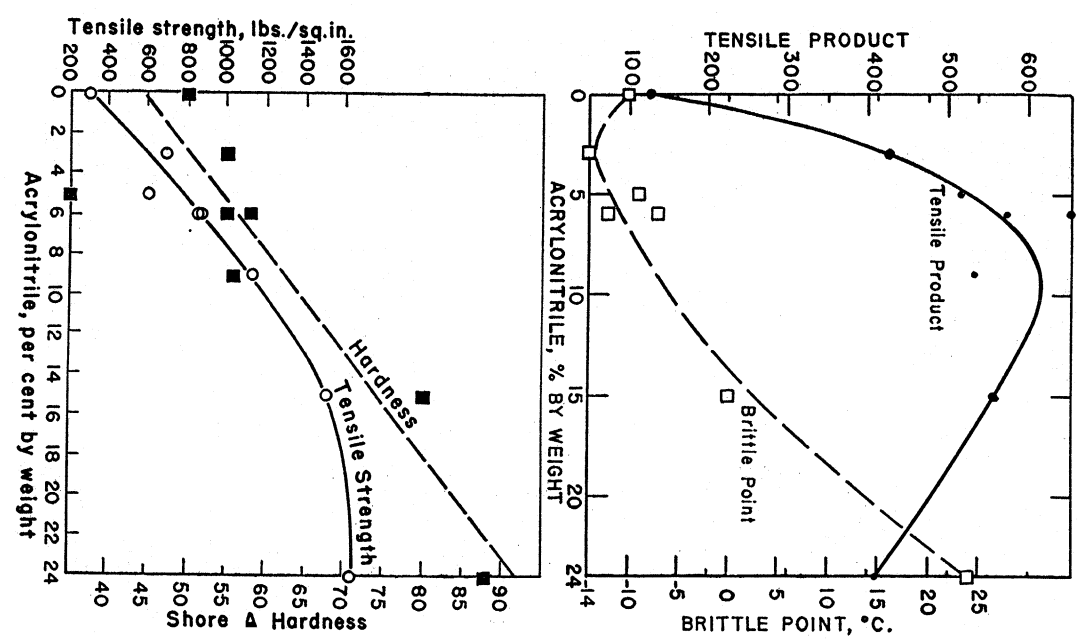

Figure 1. Effect of Acrylonitrile on Tensile Product, Brittle Point, Tensile Strength, and Hardness of Vulcanizates

Table II. Effect of Catalyst, Catalyst Concentration, and Time of Polymerization[a]

Expt. No.	Triton K 60, G.	Tergitol No. 4, G.	Catalyst: H_2O_2, ml.	Catalyst: Benzoyl peroxide, g.	Catalyst: Ammonium persulfate, g.	Polymerization: Temp., ° C.	Polymerization: Time, hr.	% Yield of Copolymer	Vulcanization: Time, min.	Vulcanization: Temp., ° C.	Tensile Strength, Lb./Sq. In.	Elongation, %	Shore A Hardness	Brittle Point, ° C.	Tensile Product	% Gain in Wt. after Immersion in Toluene-Heptane
3	1.5	0	12	0	0	65.6	3.5	90	90	148	600	610	45	−12	366	..
12	1.5	0	30	0.5	0	65.6	8.75	91	240	148	560	440	54	− 8	247	..
11	0	2	2.35	0	0	83–91	1.75	93	180	148	690	620	55	−14	427	..
28	1.5	0	15	0	0	83	3	94	300	148	560	430	60	−12	241	17.4
29	0	2	0	0	[b]	70	2.75	87	240	148	510	600	55	−10	306	14
30	1.5	0	0	0.85	0	70	1.75	86	..	..	..	..	..	..	..	..
31	0	2	0	0	0.25	70–92	0.33	96	240	148	510	330	56	−10	168	14[c]
32	0	2	0	0	0.1	70–92	0.75	95	240	148	570	430	53	−12	245	14.5
33	0	2	0	0	0.05	80–92	0.5	97	240	148	520	380	55	−11	197	14.2[c]
34	0	2	0	0	0.05	70	4	96	120	148	440	600	50	−10	264	20.8[c]
35	0	2	0	0	0.1	60	7.25	7	...	..	..	..	..	..	..	..
36	0	2	0	0	0.014	83–92	1.1	81	240	148	590	630	47	−12	372	23.6
37	0	2	0	0	0.1	60	15	53	240	148	650	610	56	−16	396	26.7
38	0	2	0	0	0.007	83–92	1.25	85	180	148	590	730	48	−13	431	19.1
39	0	2	0	0	0.003	83–89	2.5	76	180	148	730	930	50	−16	678	26.7
40	0	2	0	0	0	83	7.25	0	..	..	..	..	..	..	..	..

[a] Polymerization mixtures included 94 g. ethyl acrylate, 3 g. acrylonitrile, 3 g. allyl maleate, 300 ml. water, and 0.1 g. dodecyl mercaptan (no mercaptan was used in expt. 12). The polymers were soft and elastic with the exception of that obtained in expt. 30.
[b] Catalyst was 0.85 g. $NaBO_3.4H_2O$. [c] Vulcanizate was weakened.

vulcanized polymer decreased, the tensile strength increased, the ultimate elongation decreased, the brittle point (*9*) was raised, and the vulcanizate became harder. The copolymers obtained from monomer mixtures containing 10% or more of allyl maleate were relatively tough and inelastic and were unsuitable for milling. The effects mentioned above could be attributed to increased cross linkage or increased amounts of acrylonitrile or both.

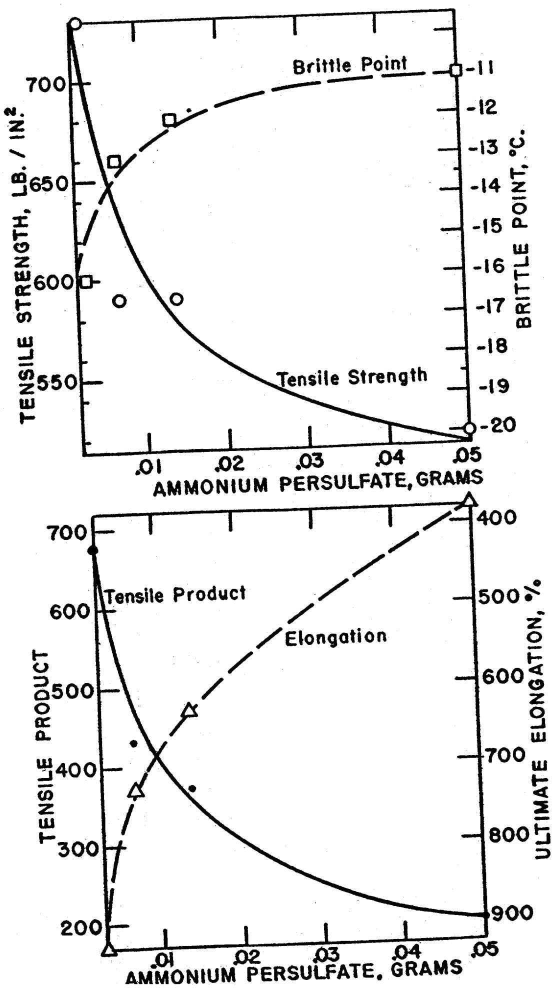

Figure 2. Effect of Ammonium Persulfate on Tensile Strength, Brittle Point, Tensile Product, and Ultimate Elongation of Vulcanizates

In the absence of acrylonitrile, both the tensile strength and ultimate elongation decreased as the proportion of allyl maleate was increased (experiments 22 to 27). In one series (experiments 9 to 21) the proportion of allyl maleate was kept constant and various amounts of acrylonitrile were used. The effect of increasing proportions of acrylonitrile may be summarized as follows: Resistance to hydrocarbons increased; the brittle point was raised (after an apparent initial drop); hardness and tensile strength increased; and ultimate elongation increased up to about 5% acrylonitrile and then decreased (Figure 1). The over-all effect of acrylonitrile seems beneficial, particularly when used as approximately 3 to 9% of the monomer mixture.

POLYMERIZATION CATALYSTS

Several conclusions were drawn regarding the relative merits of hydrogen peroxide, benzoyl peroxide, sodium perborate, and ammonium persulfate as catalysts (Table II). Hydrogen peroxide, which has the advantage of not leaving nonvolatile materials in the polymer, was moderately satisfactory. It was not so active or effective, however, as benzoyl peroxide or ammonium persulfate. Benzoyl peroxide was an active catalyst and was used in some instances (Table I, experiments 8, 10, and 12; Table II, experiment 30) when hydrogen peroxide seemed ineffective. Benzoyl peroxide, however, appeared to promote ef-

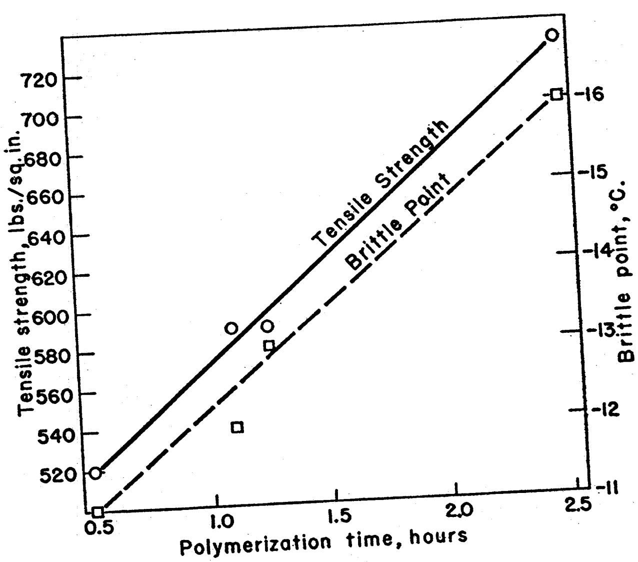

Figure 3. Effect of Polymerization Time on Tensile Strength and Brittle Point of Vulcanizates

Table III. Effect of Methyl Methacrylate[a]

Expt. No.	Monomers, G. Ethyl acrylate	Monomers, G. Methyl methacrylate	Ammonium Persulfate, G.	Polymerization Temp., ° C.	Polymerization Time, hr.	Polymerization Yield, %	Characteristics of Polymer	Vulcanization Time, min.	Vulcanization Temp., ° C.	Tensile Strength, Lb./Sq. In.	Elongation, %	Shore A Hardness	Tensile Product
41	92	5	0.020	76–93	2	95	Elastic, rubbery, tough	120	148	370	440	51	163
42	87	10	0.025	80–95	2.33	94	Fairly elastic, tough	120	148	680	570	51	387
43	77	20	0.055	74–92	2	95	Tough, hard	60	148	1200	390	65	468

[a] Polymerizations were carried out in presence of 3 g. allyl maleate, 300 ml. water, 2 g. Tergitol Penetrant No. 4, and 0.10 ml. dodecyl mercaptan.

Table IV. Effect of Solvents on Sulfur-Vulcanized Acrylic Resin (Sample 14) after Immersion for 4 Days

Solvent	Increase in Wt., %	Properties[a]	Dimensions, In.[b] Length	Width	Thickness
Acetone	26.5	W	3 1/4	3/4	0.052
Toluene	87.0	W	3 1/8	3/4	0.052
1,4-Dioxane	145.0	W	3 1/2	1	0.053
Ethyl acetate	19.2	Sl W	2 7/8	3/4	0.035
Butyl acetate	125.0	W	3 1/8	7/8	0.042
Cyclohexanol	18.5	E, S	2	1/2	0.032
Methanol	22.0	W	2	1/2	0.032
Ethanol	17.0	W	2	1/2	0.032
n-Butyl alcohol	16.5	W	2	1/2	0.032
Isopropyl alcohol	16.0	Sl W	2	1/2	0.032
Methyl lactate	314.0	W	3 3/8	3/4	0.050
Methyl acetate	10.0	S	2	1/2	0.032
Carbitol	58.0	W	2	1/2	0.032
Isoamyl alcohol	14.0	S	2	1/2	0.032
Water	19.0	E, S	2	1/2	0.034
Sulfuric acid, 30%	0.3	E, S	2	1/2	0.034
Sulfuric acid, 3%	8.0	E, S	2	1/2	0.032
Sodium chloride, 10%	1.6	E, S	2	1/2	0.034
Sodium carbonate, 2%	9.5	E, S	2	1/2	0.034
Hydrogen peroxide, 3%	100.0	W	2 1/2	5/8	0.043
Sodium hydroxide, 1%	6.2	E, S	2	1/2	0.033
Sodium hydroxide, 10%	0.7	E, S	2	1/2	0.034
Nitric acid, 10%	100.0	W	2 1/2	5/8	0.041
Hydrochloric acid, 10%	0.3	E, S	2	1/2	0.032

[a] W = weak, S = strong, E = elastic, Sl = slightly.
[b] Original dimensions were 2 × 0.5 × 0.0032 inch.

Table V. Effect of Compounding Formula and Carbon Black on Properties of Vulcanizate[a]

Expt. No.	Vulcanization Method	Carbon Black, G. Furnex Beads	Carbon Black, G. Micronex Beads	Min. of Cure at 148° C.	Tensile Strength, Lb./Sq. In.	Elongation at Break, %	Shore A Hardness	Brittle Point, ° C.
14-1	Formula 1[b]	15	0	180	420	810	40	..
14	Formula 1[b]	30	0	180	850	770	55	−12
14-2	Formula 1[b]	45	0	180	740	630	64	− 9
14-3	Formula 1[b]	60	0	240	660	480	75	− 6
14-4	Formula 1[b]	40	20	180	1090	370	71	− 9
14-5	Formula 1[b]	100	0	120	780	320	85	− 6
14-6	Formula 1[b]	0	30	180	860	650	60	..
14-7	Formula 2[c]	60	0	120	1050	360	81	− 4
14-8	Formula 3[d]	60	0	180	1380	300	84	− 6
14-9	Formula 4[e]	60	0	180	1010	420	73	− 7

[a] Copolymer (100 g. of material produced in expt. 14, Table I) used contained 91% ethyl acrylate, 6% acrylonitrile, 3% allyl maleate.
[b] 5 g. ZnO, 0.5 g. Captax, 2 g. stearic acid, 2 g. sulfur, 1 g. Tuads.
[c] 5 g. ZnO, 3 g. stearic acid, 10 g. red lead, 6 g. benzoquinone dioxime dibenzoate.
[d] 5 g. ZnO, 3 g. stearic acid, 2 g. quinone dioxime, 10 g. red lead.
[e] 5 g. ZnO, 3 g. stearic acid, 6 g. lead peroxide, 2 g. quinone dioxime.

fects, such as insolubility and toughness, that are sometimes attributed to cross linkage. Sodium perborate was used in only one experiment, but it seemed to be less active than benzoyl peroxide and ammonium persulfate and to have no particular advantage. Ammonium persulfate appeared to have several advantages over the other catalysts; only a small quantity was required, and the polymerizations initiated with this catalyst proceeded smoothly and evenly. Moreover, ammonium persulfate appeared to have no tendency to promote the production of inelastic and tough polymers.

Concentration of Ammonium Persulfate. Several emulsion polymerizations (Table II, experiments 33, 36, 38, 39, and 40) were carried out to determine the effect of concentration of ammonium persulfate on properties of the vulcanizate. Although no appreciable amount of polymerization occurred at 83° C. in 7.25 hours in the absence of a catalyst, as little as 0.003 gram of catalyst (0.003% of the monomer mixture) was employed satisfactorily in experiment 39. Not only was it possible to carry out the polymerization with small proportions of ammonium persulfate, but the quality of the vulcanizates seemed to be inversely proportional to the amount of catalyst. The brittle point, tensile strength, ultimate elongation, tensile product, and polymerization time varied markedly with small changes in concentration of ammonium persulfate when the concentration was less than about 0.015% of the monomer mixture (Figure 2). Tensile strength, brittle point, and ultimate elongation were approximately straight-line functions of the time required for virtually complete polymerization for this series of experiments (Figure 3).

Comparison of experiments 31 and 32 indicates that improved vulcanizates are obtained also by using less ammonium persulfate in the polymerization at 70° to 92° C.

OTHER VARIABLES

Mercaptans. Although the data are not in complete agreement (Table I, experiments 5, 6, 11, and 12; Table II, experiments 3, 11, and 12) and definite conclusions cannot be drawn, mercaptans having approximately 12 carbon atoms appeared to have a beneficial effect upon the copolymerization. When mercaptan was omitted, usually more catalyst and time were re-

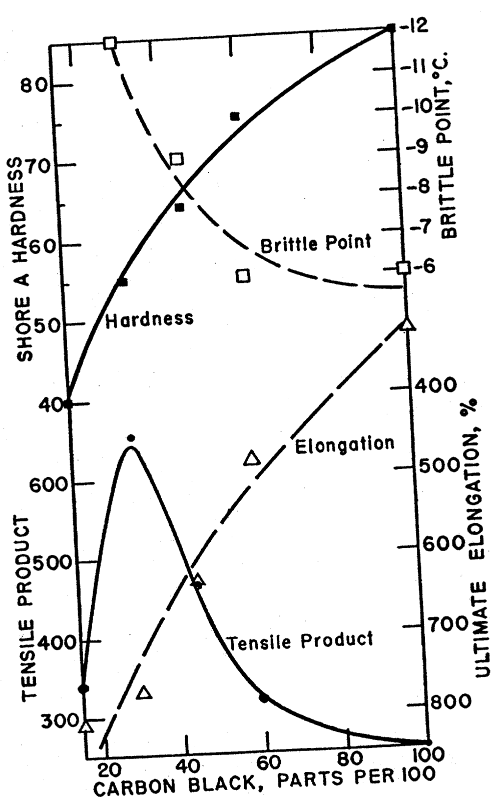

Figure 4. Effect of Carbon Black on Physical Properties of Vulcanizates

Table VI. Effect of Curing Time on Properties of Vulcanizates

No.	Properties	Curing Time at 148° C., Min. 10	15	60	90	120	180	240	300	Vulcanization	Carbon Black, Parts
15	Tensile strength, lb./sq. in.	..	..	..	640	720	870	820	840	Standard S	30
	Ultimate elongation, %	..	..	..	700	640	660	570	620		
	Shore A hardness	..	..	..	59	57	59	55	61		
39	Tensile strength	..	..	460	..	630	730	..	..	Standard S	30
	Ultimate elongation	..	..	1060	..	960	930	..	..		
	Shore A hardness	..	..	48	..	48	50	..	..		
14	Tensile strength	..	..	550	..	720	850	..	..	Standard S	30
	Ultimate elongation	..	..	860	..	850	770	..	..		
	Shore A hardness	..	..	49	..	51	55	..	..		
14-5	Tensile strength	..	..	..	..	780	750	790	..	Standard S	100
	Ultimate elongation	..	..	..	..	320	250	270	..		
	Shore A hardness	..	..	..	..	85	88	89	..		
14-8	Tensile strength	350	320	1050	..	1240	1380	..	..	Quinone dioxime & red lead	60
	Ultimate elongation	510	540	370	..	320	300	..	..		
	Shore A hardness	72	73	75	..	78	84	..	..		

quired for the polymerization and curing, the Shore hardness and brittle point were higher, and the tensile product was lower.

TEMPERATURE. Polymerization proceeded readily at 67° C. or higher in the presence of catalysts, but at 60° it was considerably more difficult to effect the polymerization and more time was required. Although only a few experiments were suitable for indicating the effect of temperature on properties of the vulcanizate, it appears that lower temperatures have a beneficial effect (Table II, experiments 3, 28, 32, 33, 34, and 37). This is in general agreement with other observations which indicate that improved vulcanizates are obtained when the rate of polymerization is relatively low.

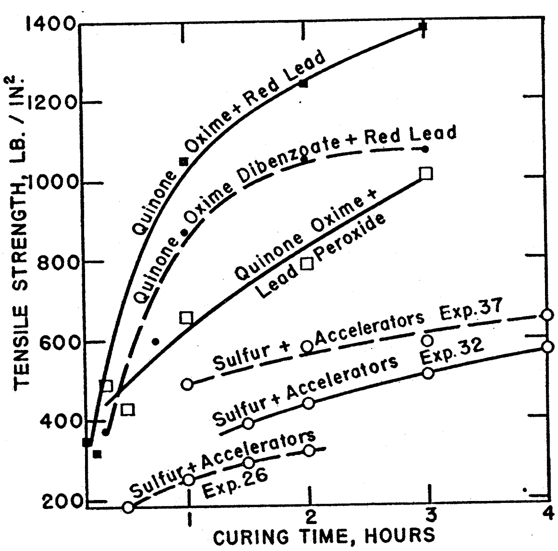

Figure 5. Effect of Curing Time on Tensile Strength of Vulcanizates

METHYL METHACRYLATE. By studying monomer mixtures containing ethyl acrylate, allyl maleate, and 5, 10, or 20% of ethyl methacrylate, it was found that the latter compound hardens the copolymer and increases the tensile strength and hardness of the vulcanizates (Table III).

VULCANIZATE PROPERTIES

SOLVENT RESISTANCE. Samples of one of the vulcanizates (experiment 14) prepared from 91% ethyl acrylate, 6% acrylonitrile, and 3% allyl maleate and vulcanized by the standard sulfur formula (Tables I and II) were immersed for 4 days in water, solvents, and various aqueous solutions, and then examined to determine the effect of this treatment. Several of the organic solvents had a weakening effect on the vulcanizate, but only five of the solvents caused great changes in the weight and dimensions of the samples (Table IV). Water and most of the aqueous solutions had little effect. Hydrogen peroxide solution and 10% nitric acid weakened the specimens, which doubled in weight after immersion in these solutions.

COMPOUNDING AND CURING. A brief study was made of the effect of carbon black on the properties of the vulcanizates. One of the copolymers (Table I, experiment 14) was vulcanized by nonsulfur methods (Table V, experiments 14-7, 14-8, 14-9). As the carbon black was increased from 15 to 100 parts per 100 parts of copolymer (Table V and Figure 4), ultimate elongation decreased, hardness increased, and the brittle point was raised. The tensile product increased as the content of carbon black was raised to 30 parts, and then decreased (Figure 4). A harder carbon black (Micronex Beads) with Furnex Beads increased tensile strength and decreased elongation without hardening the sample or raising its brittle point.

Preliminary study of nonsulfur vulcanization methods (*5*) gave promising results (Table V). Combinations of quinone dioxime, quinone dioxime dibenzoate, red lead, and lead peroxide, developed by Fisher (*3*) as agents for vulcanizing rubber, produced vulcanizates having higher tensile strengths and greater hardness than the sulfur vulcanizates. Vulcanization with the nonsulfur formulas also decreased the ultimate elongation slightly but had little effect on the brittle point.

Since only one vulcanizing or curing time is listed for each experiment in Tables I and II, additional curing data are given in Table VI and Figure 5 to indicate the effect of curing time at 148° C. on the tensile strength of the vulcanizates. These data show that after the first one or two hours, further changes in the time of curing have no pronounced effect on the tensile strength when the sulfur formula is used. It can be concluded, therefore, that in the study of polymerization conditions (Table I and II) additional curing experiments to determine the optimum time of curing at 148° C. would not have given vastly different results.

The data in Table VI and Figure 5 show also that at 148° C. nonsulfur formulas produced vulcanization more rapidly than did sulfur formulas.

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